

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No. : 10/565,767 Confirmation No. 2990  
Applicant : Yuichiro Shindo  
371 Filed : January 24, 2006  
Art Unit : 1733  
Examiner : Mark L. Shévin  
Customer No. : 00270  
Title : HIGHLY PURE HAFNIUM MATERIAL, TARGET AND THIN  
FILM COMPRISING THE SAME, AND METHOD FOR  
PRODUCING HIGHLY PURE HAFNIUM

Mail Stop RCE  
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**DECLARATION OF YUICHIRO SHINDO  
UNDER 37 CFR §1.132 TRAVERSING REJECTIONS**

1. I am the sole inventor of the above referenced application and the sole inventor of one of the cited prior art references (U.S. Patent Application Publication No. 2003/0062261 A1) upon which a rejection is based.

2. I have more than 20 years of experience in the research and development of sputtering targets, materials for sputtering targets, thin films produced by sputtering targets, and methods of making the materials, sputtering targets and thin films.

3. In an effort to traverse the rejections stated in the FINAL Office Action dated October 19, 2010, I hereby submit this Declaration to make the following facts of record in the present application:

(a) the reduced amounts of Zr content in the Hf material required by the claims of the present application cannot be achieved using the methods disclosed in my earlier application published as U.S. Patent Application Publication No. 2003/0062261 A1;

(b) the reduced amounts of Zr content in the Hf material required by the claims of the present application cannot be achieved using the iodide process disclosed by the cited publication of Murray in the ASM Handbook titled "Preparation and Characterization of Pure Metals";

(c) I was and am aware of no other method that would have been known at the time I made the present invention that could provide the reduced amounts of Zr content in Hf material as required by the claims of the present application;

(d) the present invention enabled the production of a gate-insulation film having stable permittivity that was not achievable prior to the present invention and, as a result, commercial success was achieved via the mass production of semiconductor devices; and

(e) at the time I made the present invention, one of ordinary skill in the art had no reason to reduce Zr in a Hf material beyond that taught by my earlier application published as U.S. Patent Application Publication No. 2003/0062261 A1 because conventional wisdom was that Zr mixed in high purity Hf does not aggravate the properties of semiconductors as I myself expressly disclosed in U.S. Patent Application Publication No. 2003/0062261 A1.

4. With respect to the present invention, the present application reveals Zr contents in a high purity Hf material, sputtering target and thin film of 1-1000wtppm and 1-200wtppm and discloses specific examples having 80wtppm and 5wtppm. All claims of the present application require 1-1000wtppm of Zr content and some are further limited to 1-200wtppm of Zr content.

5. The present application discloses a novel method for achieving the above results which was not previously known. High purity Hf having Zr content of 1 to 1000wtppm (or 1-200wtppm) and a purity of greater than 4N excluding gas components is produced by dissolving commercially available hafnium tetrachloride raw material ( $\text{HfCl}_4$ ) in deionized water and

thereafter performing multiple-stage organic solvent extraction to achieve a Zr content of 1000wtppm or less and then subsequently performing neutralization treatment to achieve  $\text{HfO}_2$ . The  $\text{HfO}_2$  is subject to chlorination to obtain high purity hafnium tetrachloride ( $\text{HfCl}_4$ ) which is reduced with a reducing metal such as magnesium to produce a high purity Hf sponge. The Hf sponge is subject to electron beam melting to produce the high purity Hf with extremely reduced Zr content (1-1000wtppm or 1-200wtppm). This method is neither taught by any prior art reference of record nor was known to one of ordinary skill in the art at the time the invention was made.

(a) The reduced amounts of Zr content in the Hf material required by the claims of the present application cannot be achieved using the methods disclosed in my earlier application published as U.S. Patent Application Publication No. 2003/0062261 A1

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6. My U.S. Patent Application Publication No. 2003/0062261 A1 discloses a method of producing high purity Zr and Hf with an impurity content, excluding gas components, of 100ppm by cleaning a commercially available Zr or Hf sponge raw material having a purity of 2N (99wt%) to 3N (99.9wt%) with a hydrofluoric acid and nitric acid mixture to eliminate contaminants such as organic matter and inorganic matter adhered to the surface of the raw material. Thereafter, the raw material was subjected to electron beam melting.

7. The production methods of the present invention and of my earlier U.S. Patent Application Publication No. 2003/0062261 A1 are clearly different. My earlier application disclosed cleaning based on a hydrofluoric acid and nitric acid mixture and then electron beam melting. However, with this method it is not possible to intentionally separate Zr from Hf other than an amount of Zr adhered to the surface of the raw material which is subject to the acid cleaning. This is because both elements are related elements with similar atomic structure and physical properties thereby making it extremely difficult to separate these elements. My earlier application discloses that the Zr content decreased from 25000ppm in the raw material to 3500ppm or 2400wtppm after performing cleaning with the hydrofluoric acid and nitric acid

mixture and electron beam melting. This reduction is due to the Zr adhered to the surface of the raw material being removed by the acid cleaning.

8. I performed further experiments with the raw materials disclosed in my earlier application and with the raw materials disclosed in the present application. Using the method disclosed in my earlier U.S. Patent Application Publication No. 2003/0062261 A1, I was unable to reduce Zr content below that disclosed in my earlier U.S. Patent Application Publication No. 2003/0062261 A1. When raw materials having lower amounts of Zr content were subject to acid cleaning and electron beam melting, Zr content was not able to be reduced because Zr was not adhered to the surface of such higher purity Hf material (i.e., this was already removed prior to acid cleansing). Thus, I was unable to reduce the Zr content to 1-1000wtppm or 1-200wtppm relying on the process disclosed by my earlier U.S. Patent Application Publication No. 2003/0062261 A1.

(b) The reduced amounts of Zr content in the Hf material required by the claims of the present application cannot be achieved using the iodide process disclosed by the cited publication of Murray in the ASM Handbook titled “Preparation and Characterization of Pure Metals”

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9. The “iodide process” referred to by Murray is a method of separation relying on the difference of chemical behavior between the metal being refined and impurities. It should be clearly understood that it is extremely difficult to separate Zr from Hf because these elements have such similar chemical and physical properties. Thus, the iodide process disclosed by Murray is ineffective at reducing Zr content in an Hf material and certainly cannot be used to reduce Zr content to 1000wtppm, 200wtppm, or less.

10. I performed further experiments with the raw material disclosed in the present application having 3N (99.9wt%) purity, 5wt% (5000wtppm) of Zr content, and 500wtppm of Fe content. Using the iodide method, I was unable to reduce Zr content and Fe content. Thus, I was unable to reduce the Zr content to 1-1000wtppm or 1-200wtppm and the Fe content to 10wtppm or less based on use of the iodide process.

11. Further, although 5N purity is vaguely referenced by Murray, there is no direct link to this being possible with Hf. For example, Murray states that “some impurities are almost always carried over with the vapor phase along with the metal being purified” and that by controlling temperature, “many metallic impurities, will not be carried over”. Here, Murray admits that not “all” metallic impurities can be prevented from being carried over by the iodine to the substrate even if temperature is controlled. “Ref. 5” disclosed by Murray discloses the purity of Hf achievable with the iodide process is 98.92% and 99.22% and fails to disclose Zr content. Hf and Zr have similar chemical properties and this renders the iodide process useless in separating Zr from Hf.

12. Still further, Murray discloses a purity of zirconium (“plus hafnium”) of 99.98%. It should be understood that the content of Hf in high purity Zr is typically ignored and not included with respect to the purity determination of Zr (as shown by Murray) and that the content of Zr in high purity Hf is typically ignored and not included with respect to the purity determination of Hf. Thus, even if it were possible to achieve a purity of Hf of 5N (99.999%) via the iodide process, this purity determination would be without consideration as to Zr content (i.e. Hf “plus Zr”). This is standard in the industry as evidenced by Murray.

(c) I was and am aware of no other method known at the time I made the present invention that could provide the reduced amounts of Zr content in Hf material as required by the claims of the present application

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13. To the best of my knowledge, at the time I made the present application and currently, I am not aware of any other method that could be used to reduce Zr content in an Hf material as required by the claims in the present application. I was one of ordinary skill in the art at the time the invention was made and was unaware of Hf with such greatly reduced Zr content. This is evidenced by statements in my earlier U.S. Patent Application Publication No. 2003/0062261 A1 that “a large quantity of zirconium is contained in hafnium, and notwithstanding the fact that the separation and refinement between the two is difficult, this may be disregarded since the purpose of use of the respective materials will not hinder overall

purpose hereof” and that “It is extremely difficult to reduce Zr in high purity hafnium ... the fact that Zr is mixed in high-purity hafnium will not aggravate the properties of semiconductors, and will not be a problem.”

(d) The present invention enabled the production of a gate-insulation film having stable permittivity that was not achievable prior to the present invention and as a result commercial success was achieved by the mass production of semiconductor devices

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14. In electromagnetism, “permittivity” is the measure of how much resistance is encountered when forming an electric field in a medium. Permittivity is a measure of how an electric field affects, and is affected by, a dielectric medium. Permittivity is determined by the ability of a material to polarize in response to the field, and thereby reduce the total electric field inside the material. Thus, permittivity relates to a material's ability to transmit (or "permit") an electric field. With respect to thin films used in semiconductors, it is typically undesirable to have a film with unstable permittivity.

15. As a result of the present invention, a hafnium silicide thin film was able to be produced and used as a fine gate insulation film have stable permittivity. The achievement of stability is attributed to the hafnium sputtering target (and thin film formed thereby) having extremely reduced Zr content to the extent required by the claims of the present application. Producing a hafnium silicide film having stable permittivity was not possible prior to the present invention since the Zr content (such as the content able to be provided by my earlier U.S. Patent Application Publication No. 2003/0062261 A1) was too high. At the time the invention was made, it was not known nor could be proven that the Zr content would affect the stability of the permittivity of a hafnium silicide film. The conventional thinking at the time the present invention was made was that “the fact that Zr is mixed in high-purity hafnium will not aggravate the properties of semiconductors, and will not be a problem”. Thus, a solution to providing stable permittivity to a hafnium silicide thin film was not known prior to the present invention.

16. Based on the sputtering targets produced according to the present invention, commercial success has been achieved. To date, at least about 196 hafnium sputtering targets have been made according to the present invention and sold and used to produce a large quantity of fine gate insulation films for semiconductor devices sold throughout the world. This commercial success is attributed solely to the invention claimed in the present application.

(e) At the time I made the present invention, one of ordinary skill in the art had no reason to reduce Zr in a Hf material beyond that taught by my earlier application published as U.S. Patent Application Publication No. 2003/0062261 A1 because conventional thinking was that Zr mixed in high purity Hf does not aggravate the properties of semiconductors as I myself expressly disclosed in U.S. Patent Application Publication No. 2003/0062261 A1

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17. The conventional thinking at the time the present invention was made was that “a large quantity of zirconium is contained in hafnium, and notwithstanding the fact that the separation and refinement between the two is difficult, this may be disregarded since the purpose of use of the respective materials will not hinder overall purpose hereof” and that “It is extremely difficult to reduce Zr in high purity hafnium ... the fact that Zr is mixed in high-purity hafnium will not aggravate the properties of semiconductors, and will not be a problem.”.

18. Thus, even in my own earlier application (see U.S. Patent Application Publication No. 2003/0062261 A1), I teach to one of ordinary skill in the art that hafnium and zirconium are very similar in terms of atomic structure and chemical property and that the inclusion of zirconium in hafnium has never been acknowledged as a problem and can be “disregarded”. Specifically with respect to semiconductor devices, my earlier application teaches that the Zr content “will not hinder overall purpose” and “will not aggravate the properties of semiconductors”. This is opposite to that taught and required by the present application.

19. Further, even the cited publication of Murray when referring to the purity of zirconium states “zirconium (plus hafnium”. Thus, the purity of zirconium is provided as though zirconium and hafnium refer to the same element. This is consistent with conventional teachings at the time the present invention was made.

20. Based on the teachings of the cited prior art and conventional wisdom at the time the present invention was made, there is simply no obvious reason or obvious motivation to further refine Zr content in an Hf material because such refinement is extremely difficult and because no benefit was believed to be obtained by such refinement even if possible.

21. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like are punishable by fine and imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful statements may jeopardize the validity of the application on any patent issued thereon.

Yuichiro Shindo

Signature: Yuichiro Shindo

Date: 2011/4/19